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THE DIELECTRIC CONSTANT EFFECT UPON  
THE ALKALINE HYDROLYSIS OF METHYL PROPIONATE

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ABSTRACT

The kinetics of the basic hydrolysis of methyl propionate in acetone-water media has been studied at 25.00<sup>o</sup> and 35.03<sup>o</sup> C. The effect of the dielectric constant of the medium on reaction rate has been interpreted according to an equation developed by Amis. The energies of activation and logarithms of the Arrhenius frequency factor for the various reaction media have been calculated and discussed.

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A study of the rates of acid and base catalyzed ester hydrolysis as a function of the dielectric constant and ionic strength of the medium has been undertaken. A study of the acid hydrolysis of methyl propionate has been reported (1).

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(1) Hockersmith, J. L., and Amis, E. S., Anal. Chim. Acta, 9, 101 (1953).

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A study of the base catalyzed hydrolysis of the same ester under similar conditions of temperature, concentration, and media has now been initiated.

It is thought that a study of the reaction of

methyl propionate with both a cation and an anion might be of interest in consideration of present theoretical approaches to ion-dipole reactions.

#### EXPERIMENTAL

Kinetic runs were carried out in mechanically agitated, insulated water baths with mercury or toluene-mercury thermostats for temperature regulation. It was possible to maintain control within  $\pm 0.02^{\circ}$  C of the desired temperature. When necessary, ice water was passed through coils in the baths to maintain temperature. All thermometers used were calibrated against a National Bureau of Standards thermometer ruled with 0.1 degree divisions. All volumetric apparatus was calibrated and weights used were calibrated against N.B.S. weights.

Commercially available methyl propionate was dried for 24 hours over Drierite and fractionated in a precision fractionation assembly (2).

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(2) Todd, Floyd, J. Anal. Chem., 17, 175, (1945).

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The fraction used distilled between  $79.5^{\circ}$  and  $79.6^{\circ}$  C and had a refractive index of 1.3851 at  $25^{\circ}$  C and a density of .9081 at the same temperature.

Reagent grade acetone was treated with solid potassium permanganate for 48 hours and distilled. After drying for 24 hours over anhydrous potassium carbonate, the material was fractionated and the

portion distilling between  $55.7^{\circ}$  and  $55.8^{\circ}$  C was collected. The refractive index and density of this fraction were 1.3562 and .7838, respectively, at  $25^{\circ}$  C.

Freshly boiled distilled water was used to prepare all aqueous solutions, which were subsequently protected from carbon dioxide with Ascarite. Carbonate free sodium hydroxide solutions were prepared by dilution of 50% solutions, from which sodium carbonate had been removed by filtration after 24 hours of standing. Hydrochloric acid solutions were prepared by dilution of C. P. concentrated acid.

The rate of hydrolysis of methyl propionate has been studied at  $25.00^{\circ}$  and  $35.03^{\circ}$  C. The dielectric constant of the reaction medium was altered by adding various percentages of acetone to the reaction solution. By addition of the required volume of a standard solution of the base, the reaction solution was made 0.0200 M in NaOH. The desired amount of acetone was pipetted into the reaction flask, which was then filled almost to the mark with water and allowed to come to temperature equilibrium in the bath. Water solutions of methyl propionate were prepared volumetrically so that ten milliliters yielded an ester concentration of 0.0100 M in the reaction solution. Reaction was initiated by adding this ester solution at the proper temperature. The reaction solution was then brought to the mark (five hundred milliliters), and samples were withdrawn from time to time during the course of the reaction.

These fifty milliliter samples were pipetted into a measured excess of HCl, and the excess determined by titration to the emerald green end point of bromthymol blue with dilute, standard NaOH. After sampling, each reaction solution was allowed to stand overnight, after which the final concentration was determined by averaging the titres of several samples.

The rate constants were determined from the equation

$$k' = \frac{2.303}{(a-b)t} \log \frac{b(a-x)}{a(b-x)}$$

where  $a$  is the initial NaOH concentration

$b$  is the initial methyl propionate concentration

$x$  is the concentration of either reagent reacted at the time  $t$

$k'$  is the specific rate constant.

The equation was put in the form

$$k' = \frac{2.303}{C_{\infty}t} \log \frac{C_t}{C_t - C_{\infty}} = \frac{2.303}{C_{\infty}t} \log \frac{C_0}{C_0 - C_{\infty}}$$

where  $C_t$  is the concentration of NaOH at time  $t$

$C_{\infty}$  is the concentration of NaOH at the completion of the reaction

$C_0$  is the concentration of NaOH at initiation of reaction.

A plot of  $\log C_t / C_t - C_{\infty}$  versus  $t$  was made and  $k'$  determined from the slope of the resulting straight line.

$$k' = \frac{2.303 m}{C_{\infty}}$$

where  $m$  is the slope of the line.

All runs were made in duplicate and the average  $k'$  value utilized. Table I and Figure I show the data and calculation of  $k'$  for a typical run.

TABLE I

SAMPLE KINETIC RUN

Temperature: 25.00° C Solvent: 20% Acetone Ionic Strength: 0.0200  
(by volume)

Ester Conc. = .0100 M

NaOH Conc. = .0200 M

Time (sec.)	Mls. .02510 N NaOH*	$\frac{C_t}{C_t - C_\infty}$	$\log \frac{C_t}{C_t - C_\infty}$
151	11.32	2.648	.4229
249	14.04	3.114	.4933
369	16.34	3.779	.5774
548	18.63	5.044	.7028
760	20.39	7.220	.8585
1050	21.74	11.59	1.0641
1425	22.68	21.76	1.3377
$\infty$	23.66		

Slope of plot  $\log \frac{C_t}{C_t - C_\infty}$  versus  $t = 7.125 \times 10^{-4}$

$$k = \frac{(2.303) (7.125 \times 10^{-4})}{.01022} = .161$$

From the known volumes of acetone and total volume of the reaction mixture, and ignoring the error of mixing, which was negligibly small, the weight percentages of acetone in the several reaction mixtures were calculated. The dielectric constants of the mixtures were found by interpolation of the data of Akerlof (3) for acetone-water mixtures. Table II

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(3) Akerlof, G., J. Am. Chem. Soc., 54, 4125 (1928).

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gives the dielectric constants, experimental rate constants, and precisions of the rate constant determinations for the several acetone-water mixtures. The ionic strength was held constant at 0.0200 for all runs.

\*Ml. of 0.02510 N NaOH to titrate the unneutralized HCl when 19.99 ml. of 0.05526 N H Cl was added to 50 ml. portions of the kinetic run.

TABLE II

DEPENDENCE OF RATE CONSTANTS ON  
THE DIELECTRIC CONSTANT OF THE MEDIUM

Temperature : 25.00° C.

Ionic Strength: 0.0200

Wt. % Acetone	Dielectric Constant	k'	Average % precision
0.00	78.54	0.185	0.9
8.03	74.1 <sub>5</sub>	.172	0.3
16.42	69.2 <sub>5</sub>	.157	1.7
25.20	63.9 <sub>8</sub>	.136	0.4
34.39	58.1 <sub>6</sub>	.114	0.4
44.00	52.0 <sub>9</sub>	.093	0.3
54.09	45.5 <sub>9</sub>	.078	0.0
64.70	39.6 <sub>0</sub>	.068	0.7

Temperature: 35.03° C.

Ionic Strength: 0.0200

Wt. % Acetone	Dielectric Constant	k'	Average % precision
0.00	74.8 <sub>1</sub>	0.342	0.5
7.94	70.7 <sub>4</sub>	.305	0.6
16.26	65.9 <sub>5</sub>	.279	2.5
24.97	60.9 <sub>2</sub>	.236	1.3
34.11	55.5 <sub>8</sub>	.199	1.3
43.71	49.7 <sub>9</sub>	.171	1.2
53.81	43.4 <sub>9</sub>	.144	1.9
64.43	37.7 <sub>8</sub>	.125	1.2

Figure II shows the plot of  $\log k'$  versus  $1/D$  for data at 25.00 and 35.03° C. The plots yield straight lines in the region of high dielectric constant. The slopes of the lines are in consonance with the prediction of the Amis-Jaffe equation for a reaction between a negative ion and a dipolar molecule (4). From the

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(4) Amis, E. S., "Kinetics of Chemical Change in Solution", The Macmillan Co., New York, 1949, p.

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equation

$$\log k'_{(D=D)} = \log k'_{(D=\infty)} - \frac{Z e \mu}{2.303 D k T r^2} \quad (5)$$

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(5) Amis, E. S., J. Chem. Ed., 30, 351 (1953).

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where  $k'_{(D=D)}$  is the velocity constant for dielectric constant  $D$

$k'_{(D=\infty)}$  is the velocity constant at reference dielectric infinity

$\mu$  is the dipole moment of the molecule

$Z$  is the valence of the ion

$e$  is the electronic charge

$k$  is the Boltzman constant

$r$  is the distance of approach necessary for reaction of the ion and the molecule.

the distance  $r$  can be calculated. According to theory,  $r$  corresponds roughly to the radius of the intermediate complex in the reaction, and, hence, should be of the magnitude of a molecular dimension. The slope of the



plot of  $\log k'$  versus  $1/D$  is

$$s = \frac{Z e \mu}{2.303 k T r^2}$$

and

$$r = \sqrt{\frac{Z e \mu}{2.303 s k T}}$$

Taking the moment for methyl propionate to be 1.8 Debye units (6),  $r$  was found to be  $0.92 \text{ \AA}$  at  $25.00^\circ$  and  $0.88 \text{ \AA}$

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(6) Hockersmith, J. L., and Amis, E. S., *Anal. Chim. Acta*, 9, 106 (1955).

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at  $35.03^\circ$ . Similar obedience to this equation has been found for the acid hydrolysis of ethyl acetate (7) and

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(7) Nair, P. M., and Amis, E. S., *Anal. Chim. Acta*, 9, 111 (1953).

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methyl propionate (6) and for the reaction of thio-sulfate ion with ethyl bromomalonate (8).

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(8) Branch, W. J., and Amis, E. S., accepted for publication in *J. Chem. Phys.*

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The energies of activation and logarithms of the Arrhenius frequency factor for this reaction are given in Table III. The energies were calculated from the integrated form of the Arrhenius equation stated as follows:

$$\log k_2/k_1 = \frac{\Delta E}{2.303 R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

TABLE III

ENERGIES OF ACTIVATION & ARRHENIUS FREQUENCY FACTORS

Ionic Strength: 0.0200

Average Wt, % Acetone	Interval 25.00 - 35.03° C. E (calories)	Log B Interval 25.00 - 35.03° C
0.0	11,200	7.46
8.0	10,400	6.85
16.3	10,500	6.87
25.1	10,000	6.47
34.2	10,100	6.48
43.9	11,100	7.10
54.0	11,100	7.06
64.6	11,100	6.97

The logarithms of the frequency factor were calculated from the equation:

$$\log Z = \frac{T_2 \log k_2' - T_1 \log k_1'}{T_2 - T_1} .$$

The values obtained for both  $\Delta E$  and  $\log Z$  correspond to those commonly found for basic ester hydrolysis.

25.00 °C    16.42 % Ar tone    Ionic Strength: 0.0200

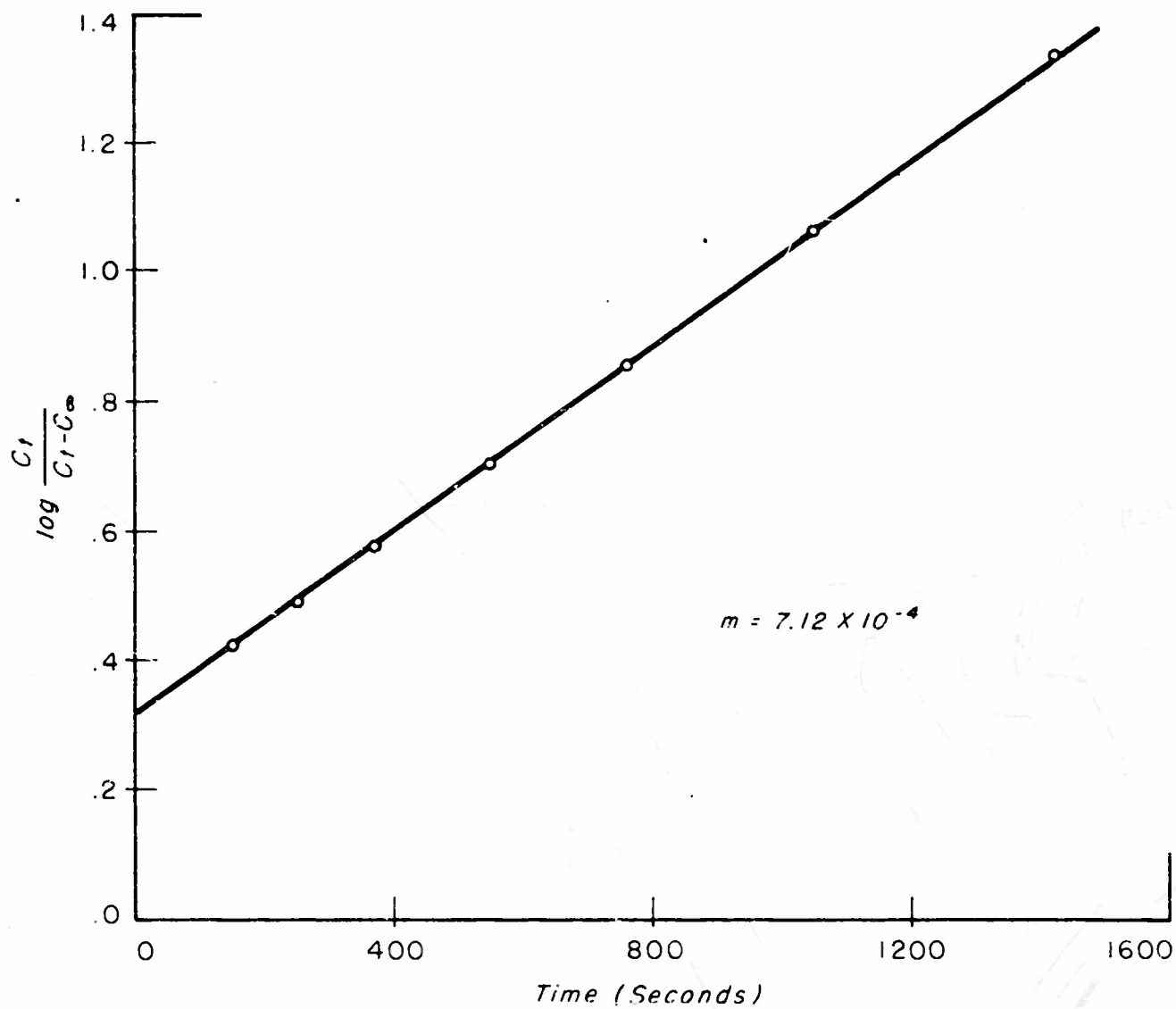


FIGURE I

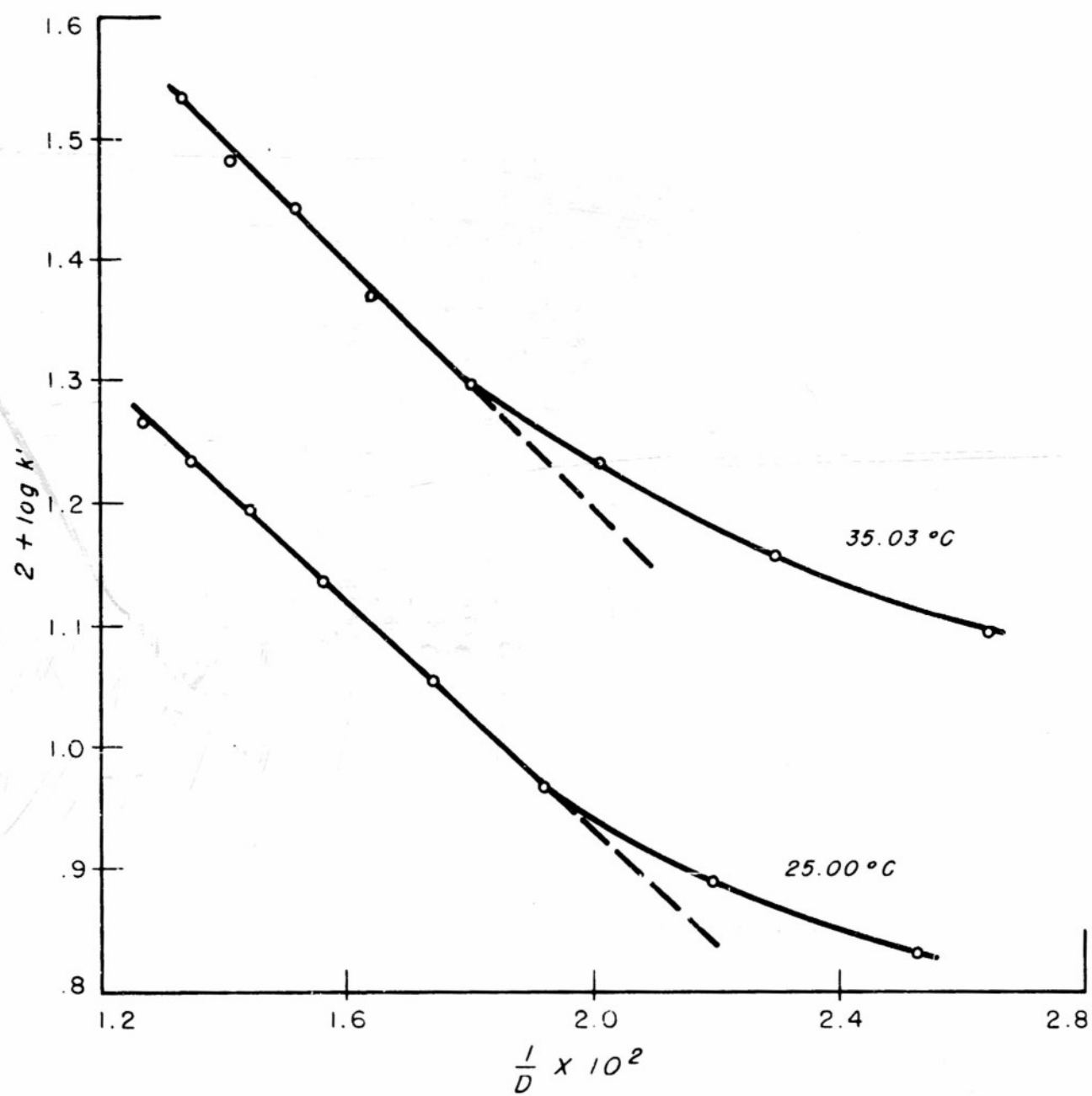


FIGURE 2